Gold in Photography

EVOLUTION FROM EARLY ARTISTRY TO MODERN PROCESSING

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For well over a century gold has played an important part in the development of the photographic process. This paper reviews the usefulness of gold in photography from its early days as a toner to its present day use as an emulsion sensitiser.

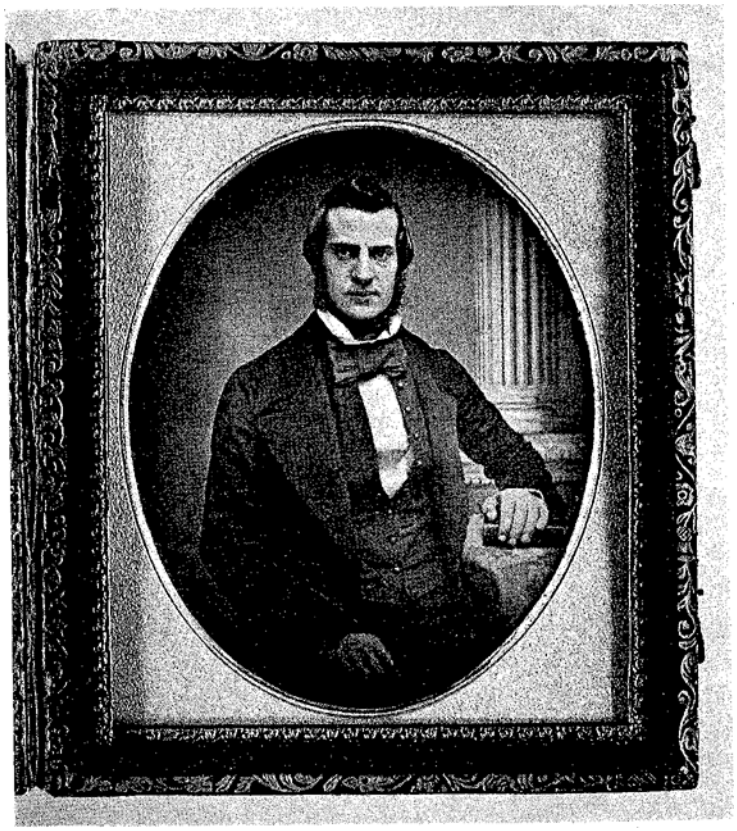
As is generally well known, conventional photographic materials rely on the ability of silver salts to be reduced after exposure to light, by the chemical action of developers, to an image of silver. A paper or film support is coated with an emulsion of minute crystals of silver halide suspended in gelatin. (This is not in fact an emulsion in the correct colloid science sense, but the word is commonly used in the industry). After a short exposure to light no visible effect is produced in the emulsion, but an invisible change occurs producing a latent image. This image must then be developed to obtain a visible image.

Silver is unique in this respect since the salts of other metals near to silver in the periodic table such as mercury and copper, although photosensitive, are either low in sensitivity or are difficult to develop, or else produce a relatively unstable latent image.

Salts of elements such as gold and palladium are not generally used as photosensitive components but they do play an important role in the photographic process, having a number of uses. Probably the most important use of gold photographically is for sensitising an emulsion, although the toning effect is most widely known.

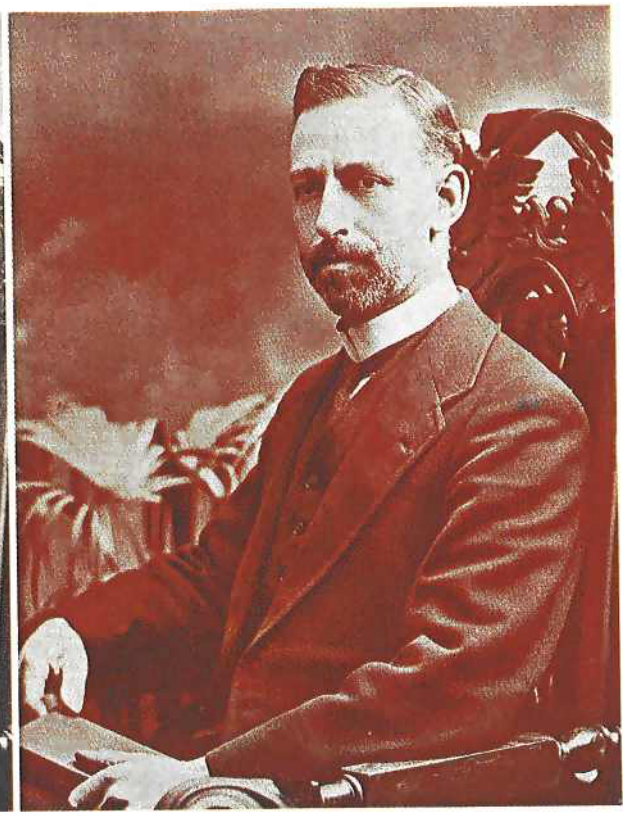
Gold Toning

Gold has been used in photography almost since the birth of photography itself. The first person to suggest its use was the French physicist Fizeau in



In 1839 Louis Daguerre devised the first successful photographic process. A silver coated metal plate was sensitised with iodine and bromine vapours and was exposed in a camera for several minutes. After removing unreacted silver halides, mercury vapour was applied to the surface of the exposed plate to render the image visible as a whitish silver amalgam against the silver background. The plate was finally toned in a warm solution containing gold chloride to improve the image and to increase its stability. This daguerrotype, reproduced by courtesy of the Kodak Museum at Harrow, dates from about 1850. The plate was usually covered by a decorative mask and was housed in a leather-covered plush-lined case

An early portrait photograph reproduced on a modern bromide paper and subsequently sulphide-toned. The brown 'sepia' tones are typical of those produced in the days when this process was popular



The same sulphide-toned print which has since been gold-toned. The brown tones have changed quite dramatically into a brilliant red colour, the image now consisting of a double sulphide of gold and silver

1840, who proposed the use of gold chloride for toning daguerreotypes. Louis Daguerre had invented the first practical process for producing camera pictures, involving the exposure of a silvered copper plate sensitised by the direct action of iodine and bromine and then the development of the plate with mercury vapour. Unreacted iodide and bromide were removed in potassium cyanide or hypo solution to leave an image of a silver-mercury amalgam. The gold toning process greatly enhanced the beauty of daguerreotypes and it also improved their permanence. Daguerreotypes were initially used for pictures of buildings and scenery, but in 1840 Goddard of London improved the process by using silver bromide and silver iodide. Much shorter exposures were required and so portrait photographs became popular, with studios opening in London, New York and Philadelphia.

Modern photographic materials stem from the work of William Henry Fox Talbot, an Englishman, who has been credited with the invention of the negative-positive process. His experiments with paper coated with salt and then brushed over with silver nitrate solution gave papers which were not very light sensitive, and exposures of an hour or so were required to produce a visible print-out image. It was when he made the discovery that a barely visible image could be developed into a much stronger image that reasonable exposure times could be considered.

Print-out images produced by the Fox Talbot process, and by other processes since, were not only unstable but were weak and unpleasant in colour compared with modern photographs. Following on from its use in toning daguerreotypes, gold was therefore used to improve the image of these prints.

Gold toning persisted for many years until print-out images were replaced by developed silver images. Even then, the striking results achieved by the toning of silver prints met with particular favour at photographic exhibitions. The images produced by the more modern materials were much blacker and much more stable than those previously obtainable, thus making gold toning more of a treatment for special effects rather than a necessity.

Many patents have been granted for different gold toning bath formulae (1) and articles outlining the technique have appeared from time to time in photographic periodicals (2). The toning bath consisted basically of a solution containing 0.1 per cent gold chloride and 1 per cent potassium or ammonium thiocyanate. Different effects could be

produced according to the nature of the original print. If a black-and-white warm tone print or transparency was immersed in a solution of a gold salt, the image turned a rich bluish-purple colour. However, cold tone bromide and chloride papers showed a much less marked effect and, if anything, turned a bluish-grey. Best results were achieved with warm coloured prints obtained by over-exposing and developing in a dilute developer solution. A sulphide-toned original on the other hand would turn a brilliant chalk red colour when treated with a gold toner, the image consisting of a double sulphide of gold and silver. This tone was also achieved most easily as a rule with prints which had been over-exposed and developed in a dilute solution.

The toning process not only produced a change in colour but also gave a more permanent image than the original silver image. This fact can be put to good use today as will be seen later.

In 1921 Formstecher (3) published the results of his studies on the mechanism of gold toning. He found that the reaction was of a purely electro-chemical nature and could be expressed by the simple equation:

$$Ag + Au^{+} \rightarrow Ag^{+} + Au.$$

When trivalent gold salts are used, the following equation applies:

$$3Ag + Au^{3+} \rightarrow 3Ag^{+} + Au.$$

Thus monovalent gold (aurous) salts ought to deposit three times as much gold as trivalent (auric) gold salts, and this is in fact borne out in practice since aurous salts are much more effective than auric salts.

Namias (4) showed that the highest possible substitution of silver by gold was of the order 40 to 50 per cent. If, however, a thiocyanate compound was used in conjunction with the gold salt, then the substitution increased immediately to 100 per cent.

Gold toning is, however, rarely if ever used nowadays. Modern photographic images are relatively stable, of good colour, and not really suited to such toning anyway. If the occasion arises when a monochrome print may be desirable, the more attractive alternative would be to use a dye toner or else to expose the image on to colour paper under an enlarger with the appropriate colour filtration. However, whereas this use of gold has declined in favour, other uses are becoming more prominent.

Image Stabilisation

Modern photographic films and prints that have been adequately fixed and washed are remarkably permanent. However, it is sometimes thought desirable to improve stability even further, particularly in the case of microforms which often must be kept for several decades. These materials can be subject to air pollutants such as sulphur dioxide, hydrogen sulphide and ozone, and such pollution can degrade the image by the formation of microscopic spots (5).

The silver image can be protected by treating it with a gold salt solution so as to overcoat the whole surface of the silver with a thin layer of gold. Crabtree, Eaton and Muehler (6) used gold thiourea complexes for this purpose and this treatment has been found to give excellent results even when the image contains small quantities of sulphide or iodide (7). Microfilms treated in this way are generally regarded as having archival permanence.

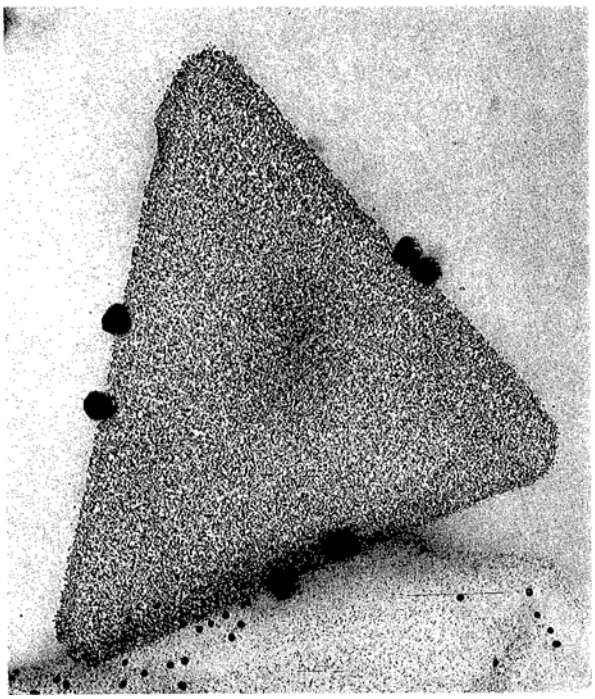
Latensification

If a photographic material is treated with a solution of certain types of chemical agents after exposure but before development, then the effective speed (or sensitivity to light) of the emulsion can be increased. This effect is known as latensification (latent-image intensification).

James and his collaborators (8, 9) of the Eastman Kodak Research Laboratories have investigated one of the most effective treatments, namely that of bathing the exposed emulsion in a solution of a gold salt for a few minutes. They showed that after latensification the silver of the latent image was replaced, at least in part, by gold. This has been confirmed by studies made on the oxidation of the latent image. Acidified potassium dichromate destroys the untreated latent image but has no effect after latensification.

Latensification has been shown to affect the rate of development (8). An untreated film approaches its maximum density slowly, whereas the latensified film rapidly attains its maximum value and remains practically constant for further development. James has also shown (8) that the efficiency of gold intensification depends on the exposure of the sensitive layer, being greater for high intensities of light than for moderate or low intensities. Development conditions also influence the effectiveness of latensification (10), being more effective with a weak developer than with a more energetic one.

Further studies by James (9) at Eastman Kodak have shown that the action of gold salt solutions on the latent image is not limited to the simple act of replacing silver by gold. Prolonged treatment with a gold solution yields a gold image which is visible in the electron microscope. Thus there is a physical development by gold producing an increase in size of the latent image centres. James has similarly shown that the formation of metallic gold is an autocatalytic reaction.



An electron micrograph showing gold development centres formed on an emulsion grain by amplification of the silver latent image by immersion in a gold salt solution. In this micrograph the original silver halide grain has been dissolved away to leave the surrounding gelatinate shell with attached gold specks **×60000**

Hamm and Comer (11) have shown in studies on crystal emulsions by electron microscopy that the size of development centres increases according to the duration of treatment with gold, but that their number remains the same.

Emulsion Preparation

The most important photographic use of gold today is undoubtedly its ability to sensitise emulsions. In order to understand how gold is used in this way a brief description of the preparation of an emulsion would seem to be appropriate.

The exact procedures for preparing photographic emulsions are closely guarded industrial secrets but the general principles of manufacture are well known (12). In outline, an emulsion is prepared by allowing silver nitrate to react with a halide such as potassium bromide in the presence of gelatin. The gelatin is first swollen by soaking it in cold water and is then dissolved in warm water. A measured amount of potassium bromide is dissolved in the solution, the appropriate quantity of silver nitrate solution is added, and the mixture is stirred continuously, giving the reaction:

$$AgNO_3 + KBr \rightarrow AgBr + KNO_3.$$

The reaction is carried out in virtual darkness in a water-jacketed kettle. The presence of gelatin prevents the precipitate of silver bromide from settling at the bottom of the kettle, thus maintaining an even suspension of silver halide crystals.

After emulsification, the emulsion is digested (or ripened) for a certain length of time, partly to allow the size of the silver halide crystals to come to equilibrium, and partly because some advantageous sensitivity changes occur. The emulsion is usually held at a temperature of from 50 to 80°C, for 30 minutes to 2 hours. It is the size distribution of the crystals that determines the photographic properties of the emulsion, and this can be altered in several ways by the emulsion chemist to suit his needs.

The next step is to wash the emulsion, otherwise a layer of potassium nitrate crystals and other impurities would form after drying on a film support. The earliest, and until recently the commonest, method of removing the impurities was to cool the emulsion so that it set to a soft jelly and then to shred the gel into small fragments called "noodles", which were treated with water to diffuse out the unwanted chemicals by osmosis. This process was very time- and water-consuming, and modern methods are mostly based on the principle of causing the gelatin to coagulate and then simply decanting the aqueous phase.

To increase its sensitivity, the emulsion is often given a second ripening period. A quantity of gelatin which has sensitising properties is added to the melted emulsion and the mixture maintained at a steady temperature for a certain length of time. This second ripening step has virtually no effect on the size of the halide, as has been shown by Chibisov and Mikhailova (13), but it does greatly increase sensitivity. The reason why certain gelatins are better than others for improving sensitivity was a mystery for some time until in 1925 Sheppard (14) of the Eastman Kodak Research Laboratories proposed the theory that these active gelatins contained sulphur sensitisers such as thiosinamin (allyl thiourea) and mustard oil (allyl isothiocyanate). He suggested that these compounds formed sensitivity centres of silver sulphide or metallic silver on the silver halide crystals.

Emulsion Sensitisation by Gold

A sensitivity effect far greater than that capable of being produced by sulphur was later found to be produced by the presence of trace amounts of gold salts in the emulsion. In 1925 Kropff of Gevaert (15) reported the possibility of sensitising an emulsion with gold chloride. Then in 1928 Carroll and Hubbard (16) tried introducing colloidal gold during the emulsion making process. Kankelwitz (17) of Kraft and Steudel used traces of gold salts in the presence of mercuric salts. Similar work was also reported by

Jenisch (18), Charriou and Valette (19), and by Schmieschek (20). However, they all found that any increase in speed could only be achieved with a corresponding increase in fog (unexposed background density), thus making the discovery commercially unusable.

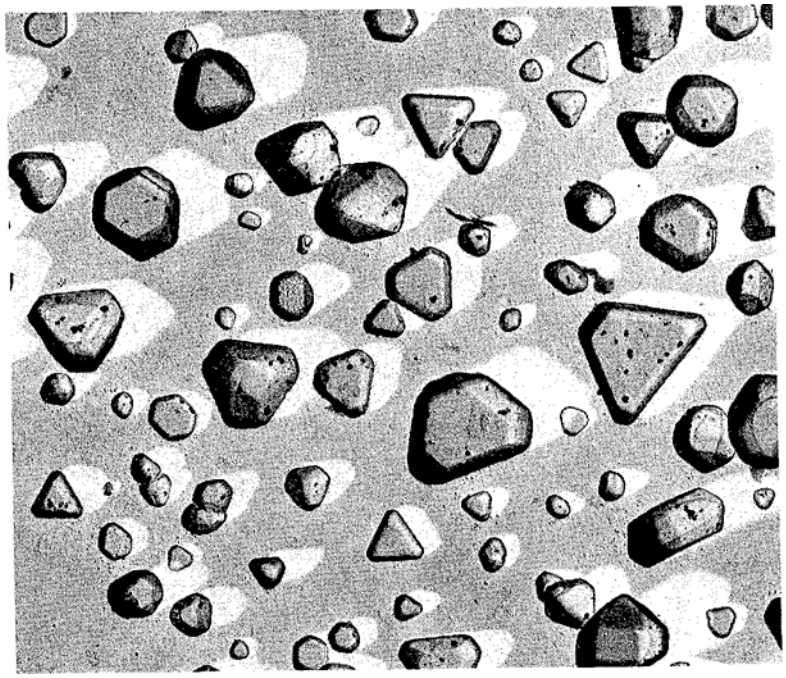
The breakthrough in sensitisation came in 1936 after Koslowsky's extensive tests on combinations of gold salts and thiocyanates (21), inspired by the advantageous effects of thiocyanates on gold toning. Working in the Agfa Filmfabrik laboratories he discovered that under certain conditions the sensitivity of an emulsion could be increased to three or four times its original value. He used complex aurothiocyanates (e.g. $NH_4Au(CNS)_2$) which he added to the emulsion after the silver or during the first or second ripening period.

Not surprisingly this discovery was exploited commercially by Agfa, together with their American subsidiary Ansco, and a number of gold sensitised films were introduced which were available without competition for a long time. Films such as SUPERPAN ULTRARAPID caused a great sensation at the time and improvements in AGFA colour films followed soon afterwards. About two years later Kodak introduced films with similar properties (PANATOMIC, SUPER-X and SUPER-XX).

Gold sensitised films were on the market for several years before any published information was available. Agfa did not file patents on the gold effect but kept it secret; however patents assigned to Kodak and other photographic firms did appear later (22) together with publications in the literature by scientists such as Faelens (23) and Mueller (24).

Koslowsky's studies showed that there was a different effect produced by very similar gold complex salts. Thus whereas $KAu(CNS)_2$ gave a considerable sensitivity increase, $KAu(CN)_2$ produced no sensitising effect whatsoever. This effect could not be explained at the time, but subsequent investigation at the Ansco Laboratories showed that gold salts whose complexes had a dissolving action on silver halide, silver sulphide and silver, were unsuitable for producing speed increases. It was proposed that with such complexes the ripening sensitivity speck was dissolved by excess cyanide before the replacement by gold could take place. Also, any gold which might have been deposited was dissolved again by the cyanide ion to form the complex cyanide. On the other hand, thiosulphate and thiocyanate ions have no dissolving effect on silver or gold so with these compounds the sensitivity effect was maintained.

Surprisingly, after more than thirty years of investigations, the mechanism of gold sensitisation is not entirely clear even to this day. Koslowsky and Mueller (25) suggested quite early on that as gold is more noble than silver, the former should be plated out on to silver sensitivity specks from dissolved aurous thiocyanate, so making the centres more efficient in forming a latent image. This theory was supported by the fact that the best sensitisation effects were achieved either during or after the chemical ripening step. The mechanism was also supported by many other observations, such as the relative effects of other noble metals. Gold is the most efficient sensitiser of them all, presumably because of the high stoichiometric yield obtained during the exchange reaction.



An electron micrograph of a carbon replica of grains of a fast negative emulsion, which received prior shadowing with gold for the estimation of grain thicknesses and for emphasis of surface features. The black specks in the grain images are of photolytic silver formed by the heavy exposure of the coating during specimen preparation ×12000

Steigmann (26) on the other hand suggested that aldehydes and amino-sugars derived from the mucopolysaccharides present in gelatin reduced the gold salt to form sensitising gold specks. Other studies by Hautot and Sauvenier (27) of the chemical composition of sensitivity specks, fog nuclei and latent image centres showed that these centres could be both metallic or ionic in character depending on how the emulsion was prepared. Many other workers in this field, including Faelens (28) of Agfa-Gevaert, have made valuable contributions to the study of the mechanism, but a thorough review of this intriguing phenomenon is beyond the scope of this article. However, the evidence does suggest that more than one mechanism may take place; the gold ion can interact with latent image silver to form gold atoms which catalyse development, and gold sulphide produced during ripening may act as positive hole acceptors with gold ions serving as effective electron traps.

Conclusion

For over a century now gold has played a very important role in the evolution of photography, from the days when photography was more of an art to the present time when emulsion preparation and coating constitutes very much of a science. Perhaps gold will find other uses in photography in the years to come.

What is certain, however, is that any developments in crystal physics which will add greater insight to the mechanism of gold sensitisation and latent image formation must benefit our future theory and practice of emulsion making.

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Soviet Research on Organogold Complexes

The chemistry of organogold complexes is attracting increasing attention in a number of countries. The strength of the effort devoted to coordination chemistry in the Soviet Union is well known, so that a report of work on gold carried out at the Moscow State University named for M. V. Lomonosov is particularly interesting. A. N. Nesmeyanov, E. G. Perevalova, K. I. Grandberg, and D. A. Lemenovskii (*Izv. Akad. Nauk S.S.S.R., Ser. Khim.*, 1974, (5), 1124–1137) have recently surveyed this field, concentrating on their own extensive researches.

Although Au^{III} complexes have been known since 1907, and Au^{I} complexes only since 1959, it is the latter on which most work is being done. Au^{I} can form π-complexes with unsaturated compounds, it can form isonitrile, ylide and carbene complexes, it can expand its coordination sphere to encompass neutral ligands such as phosphines, and it forms compounds with Au-Au bonds, e.g. polynuclear Au^{0} clusters.

Three methods of synthesis of Au^{I} compounds are described; synthesis with the assistance of organolithium and organomagnesium compounds, the aurination of carbonyl compounds, and synthesis of one organogold compound from another. The synthesis of Au^{III} compounds is described more briefly.

Considerable attention has been paid to the effect of Au-C bonds in $RAuPR'_3$ compounds and their reactions with electrophilic reagents. The reaction of vinyl(triphenylphosphine)gold with potassium permanganate is described and the existence of tris(triphenylphosphinegold)oxonium salts is demonstrated.

$^{+}AuPR'_3$ cations show affinity for mild Lewis bases. Furthermore, systematic studies of $RAuPR'_3$ compounds disclosed new binuclear organogold cationic complexes $[R(AuPR'_3)]^{+}X^{-}$ and oxonium complexes $[(R'_3PAu)_3O]^{+}X^{-}$. The syntheses, structures and reactions of these complexes are considered in detail.

F. J. S.